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(54) Abstract Title

PRODUCTION OF ACETIC ANHYDRIDE

(57) A process for the production of acetic anhydride by carbonylation of methyl acetate and/or dimethyl ether in the presence of iridium catalyst, alkyl halide co-catalyst, at least one promoter selected from ruthenium, cadmium, osmium, rhenium, zinc, mercury, gallium, indium and tungsten and an iodide salt co-promoter in which to initiate the reaction, hydrogen is present at least initially in an amount of at least 0.5 vol% based on the carbon monoxide feed.

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PROCESS FOR THE PRODUCTION OF ACETIC ANHYDRIDE

The present invention relates generally to the production of acetic anhydride and in particular to a process for the production of acetic anhydride by the carbonylation in a substantially anhydrous liquid phase of methyl acetate in the presence of an iridium catalyst.

5 It is known from, for example EP-A-0643034 (BP Case No. 8363) and EP-A-0749948 (BP Case No. 8633), to produce acetic acid by carbonylating methanol and/or a reactive derivative thereof in a liquid containing a finite concentration of water in the presence of an iridium catalyst, a halide co-catalyst, and a metallic promoter, for example ruthenium and/or osmium. It is stated in EP-A-0643034,
10 for example, that ionic contaminants, such as, for example (a) corrosion metals, particularly nickel, iron and chromium and (b) phosphine or nitrogen-containing compounds or ligands which may quaternise in situ should be kept to a minimum in the liquid reaction composition as these will have an adverse effect on the reaction by generating I⁻ in the liquid reaction composition which has a deleterious effect on
15 the reaction rate.

It is known from, for example EP-A-0728727 (BP Case No. 8548), to produce acetic anhydride by carbonylating methyl acetate in a substantially anhydrous liquid phase in the presence of a rhodium catalyst, a halide co-catalyst and ruthenium and/or osmium as a promoter and optionally also as co-promoter a
20 Group IA iodide, e.g. lithium iodide, a quaternary ammonium iodide or a phosphonium iodide. In this process it is said that ruthenium (III) trichloride and osmium (III) trichloride were not suitable sources of promoter unless hydrogen is also present, though it is demonstrated in Example 17 that acetic anhydride is nevertheless produced in the absence of hydrogen. In view of the statement
25 regarding the adverse effect of I⁻ in the process of EP-A-0643034 it would not be

expected that iridium could be used in place of rhodium as catalyst in the process of EP-A-0728727 (8548).

Nevertheless it would be desirable to use a promoted iridium catalyst for the production of acetic anhydride by the carbonylation of methyl acetate under substantially anhydrous conditions. We have found however that using substantially pure carbon monoxide as the gaseous feedstock there is no detectable reaction. The solution to this problem we have found is to initiate the reaction in the presence of hydrogen.

Accordingly, the present invention provides a process for the production of acetic anhydride by the carbonylation of methyl acetate and/or dimethyl ether which process comprises contacting in a carbonylation reactor carbon monoxide with a substantially anhydrous liquid composition comprising methyl acetate and/or dimethyl ether, acetic anhydride, an iridium catalyst, an alkyl halide co-catalyst, at least one promoter selected from ruthenium, cadmium, osmium, rhenium, zinc, mercury, gallium, indium and tungsten, and a co-promoter selected from alkali metal iodides, alkaline earth metal iodides, metal complexes capable of generating I^- , salts capable of generating I^- , and mixtures of two or more thereof wherein at least initially hydrogen in an amount greater than 0.5 vol % based on the carbon monoxide feed is contacted with the liquid composition.

By the term "substantially anhydrous liquid" is meant a liquid in which water is completely absent or is present in an amount less than 0.1% by weight.

As the feedstock there is used either methyl acetate, dimethyl ether or a mixture of methyl acetate and dimethyl ether.

The carbon monoxide employed in the process may be essentially pure or may contain inert impurities such as carbon dioxide, methane, nitrogen, noble gases and C_1 to C_4 hydrocarbons. It is preferred that the carbon monoxide be substantially anhydrous. The carbon monoxide partial pressure may suitably be in the range from greater than zero to 40 bar, typically from 4 to 30 bar.

In the process of the present invention, the iridium carbonylation catalyst is suitably present in the liquid reaction composition at a concentration in the range 400 to 5000 ppm measured as iridium, preferably in the range 700 to 5000 measured as iridium.

The iridium catalyst in the liquid reaction composition may comprise any iridium-containing compound which is soluble in the liquid reaction composition.

The iridium catalyst may be added to the liquid reaction composition for the

carbonylation reaction in any suitable form which dissolves in the liquid reaction composition or is convertible to a soluble form. Examples of suitable iridium-containing compounds which may be added to the liquid reaction composition include IrCl_3 , IrI_3 , IrBr_3 , $[\text{Ir}(\text{CO})_2\text{I}]_2$, $[\text{Ir}(\text{CO})_2\text{Cl}]_2$, $[\text{Ir}(\text{CO})_2\text{Br}]_2$, $[\text{Ir}(\text{CO})_2\text{I}_2]^+\text{H}^-$, $[\text{Ir}(\text{CO})_2\text{Br}_2]^+\text{H}^-$, $[\text{Ir}(\text{CO})_2\text{I}_4]^+\text{H}^-$, $[\text{Ir}(\text{CH}_3)_3(\text{CO})_2]^+\text{H}^-$, $\text{Ir}_4(\text{CO})_{12}$, $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{IrBr}_3 \cdot 3\text{H}_2\text{O}$, $\text{Ir}_4(\text{CO})_{12}$, iridium metal, Ir_2O_3 , IrO_2 , $\text{Ir}(\text{acac})(\text{CO})_2$, $\text{Ir}(\text{acac})_3$, iridium acetate, $[\text{Ir}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3][\text{OAc}]$, and hexachloroiridic acid $[\text{H}_2\text{IrCl}_6]$, preferably, chloride-free complexes of iridium such as acetates, oxalates and acetoacetates which are soluble in one or more of the carbonylation reaction components such as alcohol and/or carboxylic acid. Particularly preferred is green iridium acetate which may be used in an acetic acid or aqueous acetic acid solution.

In the process of the present invention one or more promoters are present in the reaction composition. Suitable promoters are selected from ruthenium, osmium, tungsten, rhenium, zinc, cadmium, indium, gallium and mercury, and are more preferably selected from ruthenium and osmium. Ruthenium is the most preferred promoter. Preferably, the promoter is present in an effective amount up to the limit of its solubility in the liquid reaction composition and/or any liquid process streams recycled to the carbonylation reactor from the acetic acid recovery stage. The promoter is suitably present in the liquid reaction composition at a molar ratio of promoter:iridium of $[0.5 \text{ to } 15]:1$. A suitable promoter concentration is 400 to 20,000 ppm, preferably from 700 to 10,000 ppm.

The promoter may comprise any suitable promoter metal-containing compound which is soluble in the liquid reaction composition. The promoter may be added to the liquid reaction composition for the carbonylation reaction in any suitable form which dissolves in the liquid reaction composition or is convertible to soluble form. Examples of suitable ruthenium-containing compounds which may be used as sources of promoter include ruthenium (III) chloride, ruthenium (III) chloride trihydrate, ruthenium (IV) chloride, ruthenium (III) bromide, ruthenium metal, ruthenium oxides, ruthenium (III) formate, $[\text{Ru}(\text{CO})_3\text{I}_3]^+\text{H}^-$, $[\text{Ru}(\text{CO})_2\text{I}_2]_n$, $[\text{Ru}(\text{CO})_4\text{I}_2]$, $[\text{Ru}(\text{CO})_3\text{I}_2]_2$, tetra (aceto)chlororuthenium(II,III), ruthenium (III) acetate, ruthenium (III) propionate, ruthenium (III) butyrate, ruthenium pentacarbonyl, trirutheniumdodecacarbonyl and mixed ruthenium halocarbonyls such as dichlorotricarbonylruthenium (II) dimer, dibromotricarbonylruthenium (II) dimer, and other organoruthenium complexes such as tetrachlorobis (4-cymene)diruthenium(II), tetrachlorobis(benzene)diruthenium(II),

dichloro(cycloocta-1,5diene) ruthenium (II) polymer and tris(acetylacetonate)ruthenium (III).

5 Examples of suitable osmium-containing compounds which may be used as sources or promoter include osmium (III) chloride hydrate, osmium metal, osmium tetraoxide, triosmiumdodecacarbonyl, $[\text{Os}(\text{CO})_4\text{I}_2]$, $[\text{Os}(\text{CO})_3\text{I}_2]_2$, $[\text{Os}(\text{CO})_3\text{I}_3]^+\text{H}^-$, pentachloro- μ -nitrodiosmium and mixed osmium halocarbonyls such as tricarbonyldichloroosmium (II) dimer and other organoosmium complexes.

10 Examples of suitable tungsten-containing compounds which may be used as sources of promoter include $\text{W}(\text{CO})_6$, WCl_4 , WCl_6 , WBr_5 , WI_2 , or $\text{C}_9\text{H}_{12}\text{W}(\text{CO})_3$ and any tungsten chloro-, bromo- or iodo-carbonyl compound.

Examples of suitable rhenium-containing compounds which may be used as sources of promoter include $\text{Re}_2(\text{CO})_{10}$, $\text{Re}(\text{CO})_5\text{Cl}$, $\text{Re}(\text{CO})_5\text{Br}$, $\text{Re}(\text{CO})_5\text{I}$, $\text{ReCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{Re}(\text{CO})_4\text{I}]_2$, $[\text{Re}(\text{CO})_4\text{I}_2]^+\text{H}^-$ and $\text{ReCl}_5 \cdot y\text{H}_2\text{O}$.

15 Examples of suitable cadmium-containing compounds which may be used as sources of promoter include $\text{Cd}(\text{OAc})_2$, CdI_2 , CdBr_2 , CdCl_2 , $\text{Cd}(\text{OH})_2$, and cadmium acetylacetonate.

Examples of suitable mercury-containing compounds which may be used as sources of promoter include $\text{Hg}(\text{OAc})_2$, HgI_2 , HgBr_2 , HgCl_2 , Hg_2I_2 , and Hg_2Cl_2 .

20 Examples of suitable zinc-containing compounds which may be used as sources of promoter include $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{OH})_2$, ZnI_2 , ZnBr_2 , ZnCl_2 and zinc acetylacetonate.

Examples of suitable gallium-containing compounds which may be used as sources of promoter include gallium acetylacetonate, gallium acetate, GaCl_3 , GaBr_3 , GaI_3 , Ga_2Cl_4 and $\text{Ga}(\text{OH})_3$.

25 Examples of suitable indium-containing compounds which may be used as sources of promoter include indium acetylacetonate, indium acetate, InCl_3 , InBr_3 , InI_3 , InI and $\text{In}(\text{OH})_3$.

30 There is employed in the liquid reaction composition a co-promoter selected from alkali metal iodides, alkaline earth metal iodides, metal complexes capable of generating Γ , salts capable of generating Γ and mixtures of two or more thereof. Suitable alkali metal iodides include lithium iodide. Metal complexes capable of generating Γ include complexes of the lanthanide metals, for example lanthanum and cerium, and nickel, iron and chromium, suitably in ionic form, preferably in the form of their iodides. Salts capable of generating Γ are, for
35 example, aluminium and quaternary ammonium and phosphonium iodides.

A preferred co-promoter salt capable of generating I in situ is lithium iodide or $\text{Al}(\text{OAc})_2\text{OH}$.

5 The co-promoter is suitably present in amounts such that it is effective in increasing the carbonylation rate. Typically when the iridium catalyst to ruthenium promoter molar ratio is about 1:[2 to 5] the molar ratio of co-promoter (expressed as I): iridium, is suitably in the range [1 to 10]:1. The amount of such co-promoter introduced to the liquid reaction composition should be selected to take account of the presence of I from other sources because it is believed that an excessive amount of I in the liquid reaction composition may be detrimental.

10 It is possible to include in the liquid composition an additional catalyst. A preferred additional catalyst is rhodium, which may be added to the liquid reaction composition in any suitable form which dissolves in the liquid reaction composition or is convertible to a soluble form. Examples of suitable rhodium-containing compounds which may be added to the liquid reaction composition include
15 $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{CO})_2\text{I}]_2$, $[\text{Rh}(\text{Cod})\text{Cl}]_2$, rhodium (III) chloride, rhodium (III) chloride trihydrate, rhodium (III) bromide, rhodium (III) iodide, rhodium (III) acetate, rhodium dicarbonylacetylacetonate, $\text{RhCl}_3(\text{PPh}_3)_3$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. The molar ratio of rhodium to iridium catalyst may suitably be in the range [0.1 to 0.5]:1, typically [0.2 to 0.4]:1.

20 As regards the alkyl halide co-catalyst the halide moiety is suitably iodide and the alkyl moiety is suitably a C_1 to C_{10} , preferably a C_1 to C_4 alkyl group. A preferred co-catalyst is methyl iodide. Suitably the concentration of alkyl halide in the liquid reaction composition is in the range from 1 to 30% by weight, preferably from 1 to 20% by weight.

25 The liquid reaction composition will also contain acetic anhydride as the principal product of the carbonylation process.

Whilst the process may be operated in the absence of added solvent it is preferred to incorporate in the liquid reaction composition a solvent, which may suitably be a carboxylic acid and is preferably acetic acid.

30 The process may be operated batchwise or continuously, preferably continuously. Whether the process is operated batchwise or continuously it is necessary to initiate the carbonylation process by the addition of hydrogen to the liquid reaction composition. Thereafter it is preferred to add further hydrogen. This may be accomplished in continuous operation for example by feeding
35 hydrogen either continuously or intermittently either separate from or together with

the carbon monoxide. The amount of hydrogen added should be at least sufficient to initiate the carbonylation reaction and thereafter maintain the continuation of the carbonylation process. Typically the amount of hydrogen may be in the range from greater than 0.5 to 10% by volume based on the carbon monoxide feed.

- 5 The process may suitably be operated at a temperature in the range from 130 to 250°C, preferably from 170 to 200°C and a total pressure in the range from 1 to 100 barg, preferably from 20 to 50 barg.

- 10 In a preferred embodiment the present invention provides a continuous process for the production of acetic anhydride by the carbonylation of methyl acetate which process comprises feeding methyl acetate and carbon monoxide continuously and hydrogen in an amount greater than 0.5 vol % based on the carbon monoxide feed either continuously or intermittently to a carbonylation reactor containing a substantially anhydrous liquid composition comprising methyl acetate in an amount in the range from 25 to 35% by weight, acetic anhydride, a catalyst system comprising methyl iodide in an amount from 10 to 15% by weight and iridium, ruthenium lithium and rhodium in a molar ratio of [1]:[2 to 5]:[1 to 10]:[0.1 to 0.25] and in an amount from 5000 to 12000 ppm and, comprising the remainder of the liquid composition, acetic acid.

- 20 The acetic anhydride product may be recovered from the liquid reaction composition by withdrawing vapour and/or liquid from the carbonylation reactor and recovering acetic anhydride from the withdrawn material. Preferably acetic anhydride is recovered from the liquid reaction composition by continuously withdrawing liquid reaction composition from the carbonylation reactor and recovering acetic anhydride from the withdrawn liquid reaction composition by one or more flash and/or fractional distillation stages in which the acetic anhydride is separated from the other components of the liquid reaction composition such as iridium catalyst, methyl iodide co-catalyst, promoter, co-promoter, methyl acetate and acetic acid solvent which may be recycled to the reactor to maintain their concentrations in the liquid reaction composition.

- 30 The invention will now be illustrated by reference to the following Examples.

Examples 1-12 and Comparison Test 1

Experimental Method

- 35 A 300 ml Hastelloy B2 autoclave equipped with a dispersimax stirrer, a ballast vessel and a liquid catalyst injection system was used for a series of batch

anhydrous carbonylation experiments. A gas supply to the autoclave, provided from a gas ballast vessel, fed gas to the autoclave to maintain a constant pressure. The rate of gas uptake was calculated from the rate at which the pressure fell in the ballast vessel.

5 At the end of the experiment liquid and gas samples from the autoclave were analysed by gas chromatography.

For each batch carbonylation experiment the autoclave was charged with any solid promoters required ($\text{Ru}(\text{CO})_4\text{I}_2$ and LiOAc) and the main liquid charge containing acetic acid, methyl acetate, acetic anhydride and methyl iodide. The autoclave was then sealed and flushed twice with nitrogen and once with hydrogen, leaving the required partial pressure of hydrogen in the autoclave at this stage. The autoclave was then additionally charged with ca. 5 barg of the feed gas and heated with stirring (950 r.p.m.) to 185°C . Once stable at this temperature the catalyst solution, consisting of ca. 2.04g of a water solution of H_2IrCl_6 dissolved in acetic acid, was then added from the injection vessel using an overpressure of the feed gas. After catalyst injection the autoclave pressure was kept constant at 28 barg (± 0.5 barg) using the gas feed from the ballast vessel.

After gas uptake from the ballast vessel had ceased, or after a set reaction period, the autoclave was isolated from the gas supply and the reactor contents cooled to room temperature. The autoclave was vented and the vent gases sampled and analysed. The liquid reaction composition was discharged from the autoclave, sampled and analysed for liquid products and by-products. Component charges are given in Table 1, reaction conditions in Table 2, and reaction rates at appropriate %wt levels of MeOAc in Table 3.

Table 1. Reaction Compositions (weights in Grams)

Example	Autoclave			Charge			Catalyst	Injection
	Ru(CO) ₄ l ₂	LiOAc**	AcOH	MeOAc	Ac ₂ O	MeI		
1	2.438	0.266	34.352	60.030	21.150	20.010	H ₂ IrCl ₆ solution*	AcOH
2	2.439	0.270	34.312	60.072	21.105	20.050	2.048	9.994
3	2.434	0.267	34.998	60.031	21.121	20.037	2.045	9.998
CT1	2.437	-	34.327	60.226	21.108	20.100	2.045	9.919
4	2.460	0.538	33.631	59.823	21.102	20.456	2.035	9.945
5	2.439	2.698	29.880	58.435	21.161	23.400	2.042	10.026
6	6.084	1.326	28.682	59.245	21.114	21.590	2.039	9.997
7	2.457	0.537	34.052	59.809	21.117	20.466	2.036	9.994
8	6.087	1.325	28.693	59.256	21.110	21.640	2.050	9.459
9	2.424	0.537	33.573	60.190	21.127	20.462	2.041	9.986
10	2.438	0.542	48.122	59.821	6.593	20.460	2.045	9.897
11	2.432	0.538	17.984	75.012	21.159	20.603	2.044	10.008
12	2.440	0.536	63.150	30.300	21.106	20.463	2.054	9.996
							2.041	9.998

* H₂IrCl₆ solution in water contains 24.39% Ir

** LiOAc used in dihydrate form

Table 2. Reaction Conditions for Experiments @ 28 barg

Example	Gaseous Feed	ppH ₂ (barg)	%wt. Ac ₂ O	Ratio Ir:Ru:Li	%wt. MeOAc
1	CO	1.4	14	1:2:1	40
2	CO	1.4	14	1:2:1	40
3	CO	3.5	14	1:2:1	40
CT1	CO	1.4	14	1:2:0	40
4	CO	1.4	14	1:2:2	40
5	CO	1.4	14	1:2:10	40
6	CO	1.4	14	1:5:5	40
7	2%H ₂ /CO	1.4	14	1:2:2	40
8	2%H ₂ /CO	1.4	14	1:5:5	40
9	10%H ₂ /CO	1.4	14	1:2:2	40
10	2%H ₂ /CO	1.4	0	1:2:2	40
11	CO	1.4	14	1:2:2	50
12	2%H ₂ /CO	1.4	14	1:2:2	20

* initial ppH₂ fed to the reactor at room temperature

Table 3. Reaction Rates

Example	Rate @ 50% MeOAc (mol/l/hr)	Rate @ 40% MeOAc (mol/l/hr)	Rate @ 30% MeOAc (mol/l/hr)	Rate @ 20% MeOAc (mol/l/hr)
1		4.5	—	
2		4.4	—	
3		5.3	—	
CT1		~0.8	—	
4		~4.2	~0.6	
5		1.4	0.9	
6		~4.3	~0.9	
7		5.7	2.5	
8		6.0	2.8	
9		6.1	2.4	
10		16.8*	3.4	
11	~4.2	~0.8	—	
12				4.5

* High rate observed due to reaction starting in aqueous conditions.

Comparison Test 1 (CT1) is not an example according to the present invention because no co-promoter was present.

Comparison Tests 2 to 5

Examples 1 and 2 and CT1 were repeated in the absence of hydrogen at 18 barg as opposed to 28 barg and no measurable conversion to acetic anhydride was detected. Increasing the hydrogen to 0.5 vol % in the carbon monoxide feed and increasing the total pressure over the range 18 to 60 barg also resulted in no measurable conversion to acetic anhydride.

These are not examples according to the present invention because hydrogen was absent throughout. They are included only for the purpose of comparison.

Example 13

Anhydrous Carbonylation of Methyl Acetate with Ir/Cd/Li (1:5:2)

Experimental Method As previously described for Examples 1-12 except:

For each batch carbonylation experiment the autoclave was charged with any solid promoters required ($\text{Cd}(\text{OAc})_2$ and LiOAc) and the main liquid charge containing acetic acid, methyl acetate, acetic anhydride and methyl iodide. The autoclave was then sealed and flushed twice with nitrogen and once with hydrogen, leaving 1.4 barg partial pressure of hydrogen in the autoclave at this stage. The autoclave was then additionally charged with ca. 5 barg of the feed gas and heated with stirring (950 r.p.m.) to 185°C . Once stable at this temperature the catalyst solution, consisting of ca. 2.04g of a water solution of H_2IrCl_6 dissolved in acetic acid, was then added from the injection vessel using an overpressure of the feed gas. After catalyst injection the autoclave pressure was kept constant at 28 barg (± 0.5 barg) using the gas feed from the ballast vessel.

Component charges are given in Table 4, and reaction rates at appropriate %wt levels of MeOAc in Table 6.

Batch reaction run @ 28 barg CO, 1.4 barg pp H_2 14%wt. acetic anhydride, 40%wt. methyl acetate.

Table 4. Reaction Composition (weights in Grams)

Example	Autoclave		Charge				Catalyst	Injection
	$\text{Cd}(\text{OAc})_2^{**}$	LiOAc^{**}	AcOH	MeOAc	Ac_2O	MeI	H_2IrCl_6 solution*	AcOH
13	3.476	0.538	30.789	57.874	21.140	24.220	2.034	9.798

* H_2IrCl_6 solution in water contains 24.39% Ir

** LiOAc and $\text{Cd}(\text{OAc})_2$ both used in dihydrate form

Example 14 and Comparison Test 6

Anhydrous Carbonylation of Methyl Acetate with Rhodium

Rh/Ru/Li (0.4:2:2) and Rh/Ir/Ru/Li (0.4:1:2:2)

Experimental Method As previously described for Examples 1-12 except:

- 5 For each batch carbonylation experiment the autoclave was charged with any solid promoters required ($\text{Ru}(\text{CO})_4\text{I}_2$ and LiOAc) and the main liquid charge containing acetic acid, methyl acetate, acetic anhydride and methyl iodide. The autoclave was then sealed and flushed twice with nitrogen and once with hydrogen, leaving 1.4 barg partial pressure of hydrogen in the autoclave at this stage. The autoclave was
- 10 then additionally charged with ca. 5 barg of the feed gas and heated with stirring (950 r.p.m.) to 185°C . Once stable at this temperature the catalyst solution, consisting of ca. 0.200g $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (and 2.04g of a water solution of H_2IrCl_6 if required) dissolved in acetic acid, was then added from the injection vessel using an overpressure of the feed gas. After catalyst injection the autoclave pressure was
- 15 kept constant at 28 barg (± 0.5 barg) using the gas feed from the ballast vessel.

Component charges are given in Table 5, and reaction rates at appropriate %wt levels of MeOAc in Table 6.

- Batch reaction run@ 28 barg 2% H_2/CO , 1.4 barg pp H_2 , (initial pp H_2 fed to the reactor at room temperature) 14%wt. acetic
- 20 anhydride, 40% wt. methyl acetate.

Table 5. Reaction Compositions (weights in Grams)

Example	Autoclave			Charge			Catalyst		Injection		
	Ru(CO) ₅	LiOAc**	AcOH	MeOAc	Ac ₂ O	MeI	[Rh(CO) ₂ Cl] ₃	H ₂ IrCl ₆	AcOH	solution*	
CT6	2.429	0.551	35.414	59.875	21.160	20.455	0.215	-	9.985		
14	2.449	0.545	33.402	59.844	21.144	20.451	0.209	2.040	10.001		

*H₂IrCl₆ solution in water contains 24.39% Ir

**LiOAc used in dihydrate form

Table 6. Reaction Rates for Experiments run with Cd or Rh

Example	Rate @ 40% MeOAc (mol/l/hr)	Rate @ 30% MeOAc (mol/l/hr)	Rate @ 20% MeOAc (mol/l/hr)
13	3.5		
CT6	4.5	3.0	1.2
14	10.5	5.9	7.6

Comparison Test (CT)6 is not an example according to the present invention because iridium was not a component of the catalyst system. It is included only for the purpose of comparison.

Further experiments (15-17) were performed at 28 barg at conditions set out below:

Example	Autoclave Charge					Cat. Inject	
	$\text{Ru}(\text{CO})_4\text{I}_2$	LiOAc^*	AcOH	MeOAc	Ac_2O	H_2IrCl_6 solution**	AcOH
15	2.47	0.53	31.26	60.02	21.00	20.483	12.01
16		0.53	27.05	60.09	21.02	20.453	16.30
17	2.45	0.54	43.37	60.13	21.03	20.48	0

* LiOAc added in dihydrate form

** H_2IrCl_6 solution in water contains 22.26% Ir

Example	Reaction pressure (barg)	Gaseous feed	ppH_2 (barg)*	%wt. Ac_2O	Ratio Ir:Ru:Li	%wt. MeOAc
15	28	2% H_2 / CO	1.4	14	1:2:2	40
16	28	2% H_2 / CO	1.4	14	1:0:2	40
17	28	2% H_2 / CO	1.4	14	1:2:0	40

*initial pp H_2 fed into the reactor at room temperature

Example	Rate @ 39% MeOAc (mol/hr)	Rate @ 35% MeOAc (mol/hr)
15	2.8	1.6
16	0.5	0.4
17	0.1	-

Comparison of example 15 with examples 16 and 17 demonstrates that there is a synergy between ruthenium, added as $[\text{Ru}(\text{CO})_4\text{I}_2]$, and iridium, added as $[\text{H}_2\text{IrCl}_6]$, in the presence of lithium, added as $[\text{LiOAc}]$, in the anhydrous carbonylation of methyl acetate to produce acetic anhydride when hydrogen is present.

Further experiments (18-22) were performed under conditions set out below which show that $\text{Al}(\text{OAc})_2\text{OH}$ is a suitable iodide generating co-promoter for anhydrous carbonylation in the presence of iridium.

Ex	Autoclave Charge						Cat. Inject		
	$\text{Ru}(\text{CO})_4\text{I}_2$	$\text{Al}(\text{OAc})_2\text{OH}$	LiOAc^*	AcOH	MeOAc	Ac_2O	MeI	H_2IrCl_6 solution **	AcOH
18	2.45	—	—	27.36	60.00	21.00	20.4 ₈	2.294	16.50
19	2.45	0.86	—	28.67	60.12	21.06	20.4 ₇	2.278	14.65
20	2.45	0.43	—	30.05	60.00	21.02	20.4 ₈	2.296	13.95
21	2.45	—	0.54	27.76	60.00	21.01	20.4 ₇	2.293	15.54
22	2.46	—	0.26	28.02	60.14	21.00	20.4 ₉	2.279	15.41

*LiOAc added in dihydrate form

** H_2IrCl_6 solution in water contains 22.26% Ir

Example	Reaction pressure (barg)	Gaseous feed	pp H_2 (barg)*	%wt. Ac_2O	Ratio Ir:Ru:Al	Ratio Ir:Ru:Li	%wt. MeOAc
18	40	2% H_2 /CO	1.4	14	1:2:0	1:2:0	40
19	40	2% H_2 /CO	1.4	14	1:2:2	—	40
20	40	2% H_2 /CO	1.4	14	1:2:1	—	40
21	40	2% H_2 /CO	1.4	14	—	1:2:2	40
22	40	2% H_2 /CO	1.4	14	—	1:2:1	40

*initial pp H_2 fed into the reactor at room temperature

Example	Rate @ 39% MeOAc (mol/l/hr)	Rate @ 35% MeOAc (mol/l/hr)
18	1.2	0.5
19	5.7	3.3
20	3.4	1.4
21	3.8	2.6
22	4.1	2.3

A further example (23) was performed as set out below:

- 5 Example 23, combined with examples 18, 20 and 21, illustrates the trend on adding more lithium to the reaction system. With iridium and ruthenium present in the molar ratio 1:2 the rate is seen to peak with 2 moles of lithium per-iridium present. With lithium added in excess of this (as in example 23) a detrimental effect on reaction rate is observed.

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Autoclave Charge							Catalyst Inject	
Ex	Ru(CO) ₄ I ₂	LiOAc*	AcOH	MeOAc	Ac ₂ O	MeI	H ₂ IrCl ₆ solution**	AcOH
23	2.45	1.07	29.43	60.00	21.00	20.49	2.289	14.34

*LiOAc added in dihydrate form

**H₂IrCl₆ solution in water contains 22.26% Ir

Example	Reaction pressure (barg)	Gaseous feed	ppH ₂ (barg)*	%wt. Ac ₂ O	Ratio Ir:Ru:Al	Ratio Ir:Ru:Li	%wt. MeOAc
23	40	2% H ₂ /CO	1.4	14		1:2:1	40

*initial pp H₂ fed into the reactor at room temperature

Example	Rate @ 39% MeOAc (mol/l/hr)	Rate @ 35% MeOAc (mol/l/hr)
23	1.1	0.8

Claims:

1. A process for the production of acetic anhydride by the carbonylation of methyl acetate and/or dimethyl ether which process comprises contacting in a carbonylation reactor carbon monoxide with a substantially anhydrous liquid composition comprising methyl acetate and/or dimethyl ether, acetic anhydride, an
5 iridium catalyst, an alkyl halide co-catalyst, at least one promoter selected from ruthenium, cadmium, osmium, rhenium, zinc, mercury, gallium, indium and tungsten, and a co-promoter selected from alkali metal iodides, alkaline earth metal iodides, metal complexes capable of generating I^- , salts capable of generating I^- , and mixtures of two or more thereof wherein at least initially hydrogen in an
10 amount greater than 0.5 vol % based on the carbon monoxide feed is contacted with the liquid composition.
2. A process as claimed in claim 1 wherein the amount of hydrogen is in the range from greater than 0.5% to 10% by volume based on the carbon monoxide feed.
- 15 3. A process as claimed in claim 1 or claim 2 wherein the molar ratio of promoter: iridium is in the range [0.5 to 15]:1.
4. A process as claimed in any one of the preceding claims wherein the molar ratio of co-promoter (expressed as I^-): iridium is in the range [1 to 10]:1.
5. A process as claimed in any one of the preceding claims wherein the co-
20 promoter salt capable of generating I^- in situ is lithium iodide or $Al(OAc)_2OH$.
6. A process as claimed in any one of the preceding claims wherein there is included in the liquid composition rhodium.
7. A process as claimed in claim 6 wherein the molar ratio of rhodium: iridium catalyst is in the range [0.1 to 0.5]:1.
- 25 8. A process as claimed in any one of the preceding claim which process

comprises feeding methyl acetate and carbon monoxide continuously and hydrogen in an amount greater than 0.5 vol% based on the carbon monoxide feed either continuously or intermittently to a carbonylation reactor containing a substantially anhydrous liquid composition comprising methyl acetate in an amount in the range
5 from 25 to 35% by weight, acetic anhydride, a catalyst system comprising methyl iodide in an amount from 10 to 15% by weight and iridium, ruthenium, lithium and rhodium in a molar ratio of [1]:[2 to 5]:[1 to 10]:[0.1 to 0.5] and in an amount from 5000 to 12000 ppm and, comprising the remainder of the liquid composition, acetic acid.

10 9. A process substantially as hereindescribed.

10. Acetic anhydride prepared by any one of the preceding claims.

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Application No: GB 9900153.9
Claims searched: 1-8

Examiner: S.I. Ahmad
Date of search: 19 February 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.Q): C2C (CYV, CJK)
Int CI (Ed.6): C07C-51/12
Other: DATA-BASE: CAS-ON-LINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	No relevant document	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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